Issued December 16, 1912.

U. S. DEPARTMENT OF AGRICULTURE.

BUREAU OF PLANT INDUSTRY—BULLETIN NO. 265.

B. T. GALLOWAY, *Chief of Bureau.*

SOME FACTORS INFLUENCING THE EFFICIENCY OF BORDEAUX MIXTURE.

BY

LON A. HAWKINS,

Scientific Assistant, Fruit-Disease Investigations.

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BUREAU OF PLANT INDUSTRY.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Plant Industry,
Office of the Chief,
Washington, D. C., September 10, 1912.

Sir: I have the honor to transmit herewith and to recommend for publication as Bulletin No. 265 of the series of this bureau a manuscript by Mr. Lon A. Hawkins, Scientific Assistant in Plant Pathology, entitled "Some Factors Influencing the Efficiency of Bordeaux Mixture."

This paper, submitted by Mr. M. B. Waite, Pathologist in Charge of Fruit-Disease Investigations, presents the results of investigations of various methods of preparation of Bordeaux mixture and of the effect of adding to the mixture different compounds designed to increase its adhesiveness.

The results obtained are of importance where this fungicide is used and should be of special interest to cranberry and grape growers.

Respectfully,

B. T. Galloway,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

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SOME FACTORS INFLUENCING THE EFFICIENCY OF BORDEAUX MIXTURE.

INTRODUCTION.

The efficiency of Bordeaux mixture in preventing certain diseases which attack the young aerial portions of plants is dependent on several factors. Not the least among these is uniformity in the distribution of the copper compound throughout the liquid medium when the mixture is applied. That this is of importance is very apparent, for if the copper compound has settled out, even to a limited degree, part of the plant will receive a heavy coating of the fungicide, while other portions may receive none and thus be liable to infection by the fungus. Another important factor is adhesiveness, as it is obviously necessary for the fungicide to adhere to the susceptible portions of the plant if they are to be protected from fungous disease. With these requirements for efficiency in mind the questions naturally arise, By what methods can the most uniform distribution of the copper compound in the medium be obtained, and how can the adhesiveness of the mixture to the susceptible parts of the plants be increased? The present investigation deals with these two questions.

COMPOSITION OF BORDEAUX MIXTURE.

Bordeaux mixture is made up of copper sulphate and calcium hydroxid, and the rate of subsidence of the colloidal suspension of the precipitate which results from the interaction of these substances is partly dependent on the manner in which the two components are brought together. It is not necessary here to go into a detailed discussion of the chemical reactions that take place when copper sulphate and calcium hydroxid are brought together. They have been studied by Swingle,[1] Chester,[2] Sostegni,[3] Pickering,[4] and others, with various

[1] Swingle, Walter T. Bordeaux Mixture: Its Chemistry, Physical Properties, and Toxic Effects on Fungi and Algæ. Bulletin 9, Division of Vegetable Physiology and Pathology, U. S. Dept. of Agriculture. 1896.

[2] Chester, F. D. Copper Salts as Fungicides. Journal of Mycology, vol. 6, 1890, pp. 21–24.

[3] Sostegni, Livio. Sulla Composizione Chimica della Cosi detta Poltiglia Bordolese. Le Stazioni Sperimentali Agrarie Italiane, vol. 19, 1890, pp. 129–141.

[4] Pickering, Spencer U. Eleventh Report of the Woburn Experimental Fruit Farm. 1910.

conclusions as to the nature of the compounds formed. It is generally agreed that the insoluble copper compound of Bordeaux mixture, whether copper hydroxid, basic sulphate of copper, or both these compounds, is in colloidal suspension in a saturated or nearly saturated solution of calcium sulphate and calcium hydroxid.

PREPARATION OF BORDEAUX MIXTURE.

Different authors have recommended various methods for the preparation of Bordeaux mixture, with a view of obtaining the most economical and effective mixture. Millardet,[1] in describing the making of Bordeaux mixture for the first time, says:

> Dans 100 litres d'eau quelconque (de puits, de pluie, ou de rivière) on fait dissoudre 8 kilos de sulfate de cuivre du commerce. D'un autre côté, on fait, avec 30 litres d'eau et 15 kilos de chaux grasse, en pierres, un lait de chaux qu'on mélange à la solution de sulfate de cuivre.

This method of mixing, with the same formula, was adopted in America, having been first published by Scribner[2-3] in 1886. Two years later Scribner[4] recommended 4 pounds of copper sulphate and a like quantity of lime in 22 gallons of mixture, while Galloway[5] the same year recommended a formula of 6 pounds of copper sulphate and 4 pounds of stone lime to 22 gallons of water. Waite[6] in 1893 obtained good results in spraying for pear leaf-blight by using 6 pounds of copper sulphate to 50 gallons of water with just sufficient lime to react with the copper sulphate. In the same article this writer recommends the use of a stock solution of copper sulphate and a stock mixture of lime in the preparation of the fungicide. With these formulas, the method of preparation was to pour the calcium hydroxid into the copper-sulphate solution. In 1896 Galloway[7] recommended the use of two tubs, in which the copper sulphate and lime were separately diluted, each to half the volume of the Bordeaux mixture required. From these tubs the two solutions were poured simultaneously into a barrel. In the same article he recommended

[1] Millardet, A. Journal d'Agriculture et d'Horticulture de la Gironda, May 1, 1885.

NOTE.—This publication was not at hand and the quotation given was taken from the same writer's paper, entitled "Sur l'histoire du traitement du mildiou par le sulfate de Cuivre," Journal d'Agriculture Pratique, vol. 49, pt. 2, 1885, pp. 801–805, in which Millardet quotes directly from his former paper in describing the method of preparing Bordeaux mixture.

[2] Scribner, F. Lamson. Report on the Mycological Section, in the Report of the Commissioner of Agriculture for 1886, p. 100.

[3] ——— Report on the Fungous Diseases of the Grapevine. Bulletin 2, Section of Plant Pathology, Botanical Division, U. S. Dept. of Agriculture, 1886, p. 16.

[4] ——— Fungicides or Remedies for Plant Diseases. Circular 5, Section of Vegetable Pathology, Botanical Division, U. S. Dept. of Agriculture, 1888.

[5] Galloway, B. T. Treatment of Black Rot of the Grape. Circular 6, Section of Vegetable Pathology, Botanical Division, U. S. Dept. of Agriculture, 1888, p. 2.

[6] Waite, M. B. Treatment of Pear Leaf-Blight in the Orchard. Journal of Mycology, 7, 1894, pp. 333–338.

[7] Galloway, B. T. Spraying for Fruit Diseases. Farmers' Bulletin 38, U. S. Dept. of Agriculture, 1896, p. 6.

6 pounds of copper sulphate and 4 pounds of lime to 50 gallons of mixture. This last method of mixing Bordeaux has been recommended by the investigators in the Department of Agriculture and most of the agricultural experiment-station workers in the United States since that time. Some of the experiment stations, however, recommend the pouring of one component into the other, as shown by the publication of Woods and Hanson,[1] Green, Selby, and Gossard,[2] and Smith and Smith.[3] Kelhofer[4] in an account of his investigations on the preparation of Bordeaux mixture says:

Die grössten Niederschläge erzielen wir demnach bei langsamem (portionenweisem) Zusatz der Kupfervitriollösung zur Kalkmilch. Annähernd ebenso günstige Resultate werden erhalten, wenn man die Kalkmilch rasch zur Kupfervitriollösung giesst.

The copper sulphate and lime of Kelhofer's preparations were both diluted to the same volume. Two series of experiments were carried out, in one of which this volume was one-half that of the fungicide required and in the other one-fourth. Kelhofer[5–6] also added with good results small quantities of cane sugar to retard the rate of subsidence of the suspension. Kulisch[7] repeated some of Kelhofer's experiments with like results. Pickering,[8] in making common Bordeaux mixture, recommends the use of calcium hydroxid as dilute as possible to make the required quantity and the copper sulphate in concentrated solution. The copper sulphate is poured into the calcium hydroxid with very little stirring. An examination of the literature of this subject shows that the methods recommended for the preparation of a colloidal suspension of the copper compound which settles out slowly are rather varied. The problem of making a suspension which subsides slowly then resolves itself into testing the methods of mixing recommended by the different investigators to determine their comparative efficiency. Accordingly, to determine the effect on the rate of subsidence of the suspensions of some of these

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[1] Woods, Charles D., and Hansen, H. H. Paris Green Bordeaux Mixture. Bulletin 154, Maine Agricultural Experiment Station, April, 1908.

[2] Green, W. J., Selby, A. D., and Gossard, H. A. Spray Calendar. Bulletin 232, Ohio Agricultural Experiment Station, 1911.

[3] Smith, R E., and Smith, Elizabeth H. Bulletin 218, Agricultural Experiment Station of the University of California, 1911, p. 1185.

[4] Kelhofer, W. Versuch über die Herstellung der Bordeauxbrühe. Jahresbericht der Deutsch-Schweizerischen Versuchstation und Schule für Obst-Wein- und Gartenbau, vol. 8, 1897–98, p. 65.

[5] Kelhofer, W. Versuche über die Beeinflussung der Haltbarkeit der Bordeaubrühe durch Zusätze. Jahresbericht, der Deutsch-Schweizerischen Versuchstation und Schule für Obst-Wein- und Gartenbau, vol. 9, 1898–99, pp. 87–92.

[6] ——— Ueber einige Gesichtspunkte bei der Herstellung der Bordeauxbrühe. Zeitschrift für Pflanzenkrankheiten, vol. 18. Internationaler Phytopathologischer Dienst, vol. 1, no. 3, 1908, pp. 65–73.

[7] Kulisch, P. Die Darstellung haltbarer Kupferbrühen zur Bekämpfung der Peronospora. Zeitschrift für Pflanzenkrankheiten, vol. 21, 1911, pp. 382–384.

[8] Pickering, Spencer U. Op. cit., p. 56.

methods of preparing Bordeaux mixture the investigations described in the first part of this paper were planned and carried out.

EXPERIMENTS IN PREPARATION.

For the greater part of the investigation the copper sulphate and lime used were what is commonly known as chemically pure. Distilled water was used in these preparations. Later, a number of the series were repeated in order to approach commercial conditions as closely as possible, using a good grade of common stone lime, commercial copper sulphate, and tap water. The mixtures were prepared in glass-stoppered cylinders of 1-liter capacity graduated to divisions of 10 cubic centimeters. To prepare Bordeaux mixture by allowing the two diluted components to flow simultaneously into the container, two burettes of 1,000 cubic centimeters capacity were placed side by side, with the outlets connected by rubber tubes provided with pinch cocks to a single Y tube, the lower arm of which was so arranged as to project into the neck of the glass cylinder. The proper quantity of calcium hydroxid, made by slacking 3.75 grams of calcium oxid, was placed in one burette and diluted to half a liter, while in the other was placed a solution of the same volume, containing 5 grams of copper sulphate. A current of air was forced in at the bottom of the burette containing the calcium hydroxid to keep the precipitate from settling out. If the two pinchcocks were opened at the same time the milk of lime and the copper-sulphate solution flowed simultaneously into the graduated receiver, and by properly manipulating the pinchcock either component could be added to the other. This apparatus was used in preparing all mixtures in which both the lime and the copper sulphate were diluted to the same volume before bringing them together. The comparative volumes of the precipitates were determined by measuring the fall of the precipitate surface in the different mixtures during a given time interval, the graduations on the cylinders serving as convenient indexes for this purpose. The formula used in the preparation was usually that for 4–3–50 Bordeaux mixture (4 pounds of copper sulphate and 3 pounds of lime to 50 gallons of water), which is a standard formula for use on grapes and cranberries.

Effect of Different Methods of Mixing on the Rate of Subsidence of the Suspension.

The methods of mixing were as follows:

(1) Calcium hydroxid and copper sulphate were made up to 500 cubic centimeters each and allowed to flow simultaneously into the receiver.

(2) Calcium hydroxid and copper sulphate were made up to 500 cubic centimeters each and calcium hydroxid allowed to flow into the copper sulphate.

(3) Calcium hydroxid and copper sulphate were made up to 500 cubic centimeters each and copper sulphate allowed to flow into the calcium hydroxid.

(4) Calcium hydroxid was made up to 950 cubic centimeters and shaken; copper sulphate was made up to 50 cubic centimeters and poured into the calcium hydroxid.

(5) Copper sulphate was made up to 950 cubic centimeters; calcium hydroxid was made up to 50 cubic centimeters and added to the copper sulphate.

(6) Calcium hydroxid and copper sulphate were made up to 50 cubic centimeters each; the calcium hydroxid was added to the copper-sulphate solution and the mixture diluted to 1,000 cubic centimeters.

In addition to these the rate of subsidence of Woburn Bordeaux mixture, recommended by Pickering, which is made from clear lime water and copper-sulphate solution, was tested.

The results obtained in these tests were varied. Throughout the investigation, however, No. 1, the method of mixing described first by Galloway, was found to result in a suspension which subsided as slowly as any of the others, except the Woburn Bordeaux mixture. The results with No. 2 and No. 3 in most cases closely approached those with No. 1. With Nos. 4 and 5, in which one of the components in a concentrated form was poured into the other made up to nearly the volume of fungicide desired, about as good results were obtained as with No. 1, provided the mixtures were properly agitated.

When the two components were brought together in concentrated form, as in No. 6, the suspension settled out much more rapidly than with any of the other preparations. This method of making Bordeaux mixture seems therefore to be entirely unsatisfactory, as has been almost universally held by previous writers.

Effect of Varying Amounts of Agitation on the Subsidence of the Suspension.

Experiments were carried out to test the effects of varying amounts of agitation on the rapidity of subsidence of the suspension when prepared by adding one of the components in concentrated form to the other made up to nearly the quantity of solution required, as in Nos. 4 and 5. In agitating, the graduates were stoppered and shaken vigorously with an up-and-down motion, the amount of agitation being measured by the number of complete excursions made by the container during the shaking. As there was always a large air space above the liter of mixture in the graduated cylinder, a very thorough agitation could be easily obtained by this method.

EXPERIMENTS WITH CONCENTRATED LIME POURED INTO DILUTE COPPER SULPHATE.

In experiments with the concentrated lime poured into the dilute copper-sulphate solution, five mixtures were prepared: *A*, The standard solution, for purposes of comparison, was mixed by allowing the copper sulphate and calcium hydroxid, each diluted to 500 cubic

centimeters, to flow simultaneously into the 1,000 cubic centimeter graduate. The others, *B* to *E*, were prepared by pouring the lime, made up to 50 cubic centimeters, into the copper-sulphate solution diluted to 950 cubic centimeters. *A* and *B* were each shaken 5 times; *C*, 15 times; *D*, 25 times; and *E*, 35 times. The preparations were then allowed to stand one hour, when the volume of the precipitate was read on the scale of the graduate. It was found that the pre-

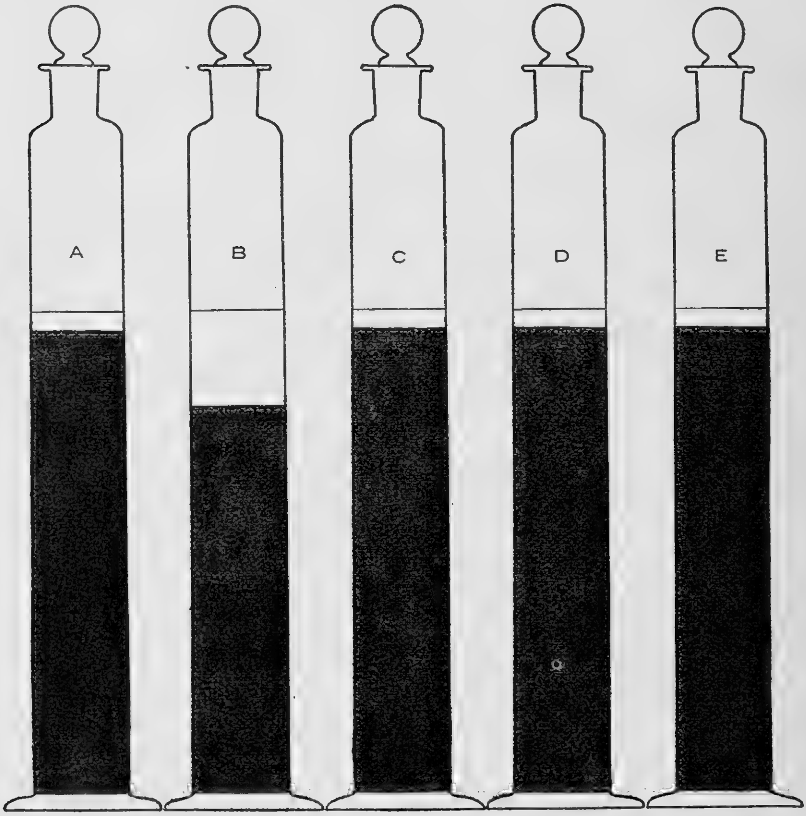

Fig. 1.—Diagram showing the effect of varying the amount of agitation of Bordeaux mixture when the concentrated lime is added to the diluted copper-sulphate solution. The shaded portion represents the precipitate after 1 hour. In *A*, the standard solution, the two components diluted to half the quantity were poured simultaneously into the container and shaken 5 times. In *B*, *C*, *D*, and *E*, the concentrated lime was poured into diluted copper-sulphate solution and shaken 5, 15, 25, and 35 times, respectively.

cipitate in *B*, shaken the same number of times as the control, settled much more rapidly than *A*, while in *C* to *E*, shaken from 15 to 35 times, the suspension subsided with about the same rapidity as in *A*. The experiments were repeated a number of times, with similar results. The average volume from three separate experiments is shown graphically in figure 1. A description of the treatment given the preparations and the results obtained are given in Table I.

TABLE I.—*Results of tests showing the effect of agitation of Bordeaux mixture when the concentrated lime is poured into the dilute copper-sulphate solution.*

Mixture used and method of preparation.	Times shaken.	Average volume of precipitate after 1 hour, as measured on scale of the graduate.
		Cubic centimeters.
A. Standard, both $Ca(OH)_2$ and $CuSO_4$ diluted to 500 cubic centimeters and allowed to flow simultaneously into receiver	5	970
B. $Ca(OH)_2$ diluted to 50 cubic centimeters and poured into $CuSO_4$ solution diluted to 950 cubic centimeters	5	805
C. Preparation same as *B*	15	970
D. Preparation same as *B*	25	970
E. Preparation same as *B*	35	970

EXPERIMENTS WITH CONCENTRATED COPPER SULPHATE POURED INTO DILUTE LIME.

In the series of experiments in which the copper-sulphate solution was made up to 50 cubic centimeters and then poured into the lime made up to 950 cubic centimeters the results were much the same as when the concentrated calcium hydroxid was poured into the dilute copper sulphate. The experiments are comparable in every way, since in both series the same quantities were used, the gradations in amount of agitation were the same, and the observations were made after the same length of time. The individual experiments were repeated a number of times, with practically the same results. An average of three, in which the preparations were made up with commercial copper sulphate and common stone lime, gave the results as shown in Table II.

TABLE II.—*Results of tests showing the effect of the agitation of Bordeaux mixture when the concentrated copper-sulphate solution is poured into the dilute lime.*

Mixture used and method of preparation.	Times shaken.	Average volume of precipitate after 1 hour, as measured on scale of the graduate.[1]
		Cubic centimeters.
A. Standard, both $Ca(OH)_2$ and $CuSO_4$ diluted to 500 cubic centimeters and allowed to flow simultaneously into receiver	5	972½
B. $CuSO_4$ diluted to 50 cubic centimeters and poured into the $Ca(OH)_2$ diluted to 950 cubic centimeters	5	703
C. Preparation same as *B*	15	836
D. Preparation same as *B*	25	916
E. Preparation same as *B*	35	900

[1] A graphic representation of these averages is shown in figure 2.

DISCUSSION OF EFFECTS OF AGITATION.

The foregoing experiments seem to show that the rate of subsidence of the suspension in Bordeaux mixture is not entirely dependent upon the manner in which the two components are brought together, but is also dependent to a certain extent on the amount of agitation

the mixture receives. For example, if the mixtures, in which one of the components in high concentration is poured into the other diluted to nearly the required volume, are sufficiently agitated, the resulting suspension will subside about as slowly as the suspension in a mixture prepared by the standard method recommended by Galloway. (See figs. 1, *C*, *D*, and *E*, and 2, *D* and *E*.) On the other hand, if mixtures

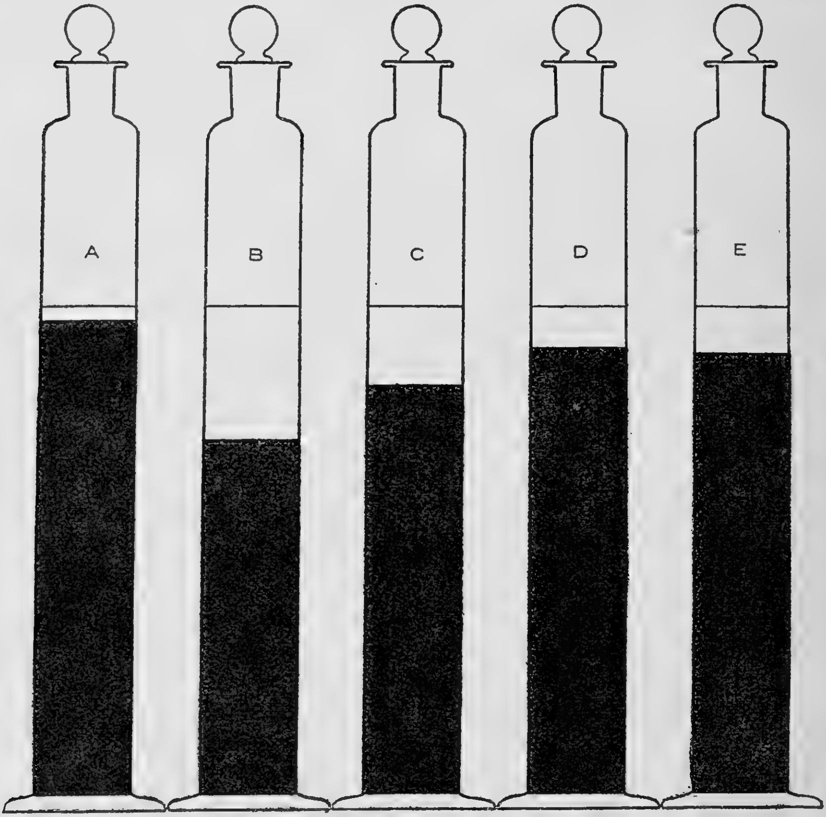

FIG. 2.—Diagram showing the effect of varying the amount of agitation of Bordeaux mixture when the concentrated copper-sulphate solution is added to the diluted lime. The shaded portion represents the precipitate after 1 hour. In *A*, the standard solution, the two components diluted to half the quantity required were poured simultaneously into the container and shaken 5 times; in *B*, *C*, *D*, and *E*, the concentrated copper-sulphate solution was poured into dilute lime and shaken 5, 15, 25, and 35 times, respectively.

prepared in this way receive only a small amount of agitation, the suspension subsides much more rapidly. (See figs. 1 *B*, and 2, *B*.) A probable explanation of this fact lies apparently in the structure of the precipitate formed when the two components of Bordeaux mixture are brought together. On this subject the work of Swingle[1] seems to be generally accepted.

[1] Swingle, Walter T. Bordeaux Mixture: Its Chemistry, Physical Properties, and Toxic Effects on Fungi and Algæ. Bulletin 9, Division of Vegetable Physiology and Pathology, U. S. Dept. of Agriculture. 1896, p. 13.

This writer has shown that when calcium hydroxid and a solution of copper sulphate are brought together small Traube cells are formed, composed of a precipitation membrane of the insoluble copper compound surrounding either a drop of calcium-hydroxid solution or a particle of the undissolved calcium hydroxid. It may be suggested that in the latter case the particles of calcium hydroxid remaining inside the precipitation membrane might weigh them down and make them settle out more rapidly than those in which no solid was present. If, however, the mixture were sharply agitated the precipitation membranes might be broken and the undissolved particles of lime could settle to the bottom without taking with them the precipitation membranes of the copper compound.

This explanation receives further support from the fact that when Bordeaux mixture is made by allowing the two dilute solutions to flow simultaneously into the container, the lime being well agitated meanwhile, the resulting suspension subsides much less rapidly than a mixture in which one of the components in high concentration is poured into the other one diluted, provided the mixtures receive only a small amount of agitation. In the case of the two components of the mixture, each diluted to half the required volume, the particles of calcium hydroxid would be suspended in a relatively large volume of liquid, and the precipitation membranes in the Bordeaux mixture made from this milk of lime should be smaller and contain less solid matter to weigh them down than if the concentrated calcium hydroxid were added in a pasty mass to the diluted copper-sulphate solution. On the other hand, the formation of thick, heavy precipitation membranes would be much less probable when the two diluted solutions were brought together than if the concentrated copper-sulphate solution were added to the diluted calcium hydroxid.

Pickering's Woburn Bordeaux mixture, as prepared in this investigation, also furnishes further evidence in support of this explanation. This mixture was prepared by adding a concentrated solution of copper sulphate to a saturated solution of calcium hydroxid which had been filtered. No undissolved calcium hydroxid and at most only a small quantity of undissolved calcium sulphate were in the mixture. Consequently, there being nothing to weigh down the precipitate, it should remain in suspension much better than the Bordeaux mixture made in the usual way. The result was as expected. The mixture was made up and stood on the table about two months, being agitated from time to time. The precipitate settled out very slowly after each agitation and never reached the stage at which it was impossible to bring it into relatively uniform suspension throughout the whole mixture. From these facts it seems fair to conclude that the slow subsidence of the suspension in the experiments in which one of the components in high concentration was

added to the other which had been diluted to nearly the required volume was due to the breaking up of the precipitation membranes and the elimination, partially at least, of the solid calcium hydroxid and calcium sulphate from the suspended precipitate. Lutman,[1] in a recently published account of his investigations of Bordeaux mixture, reaches much the same conclusions in regard to the settling out of the precipitation membranes.

ADHERENCE OF BORDEAUX MIXTURE WITH AND WITHOUT ADDED ADHESIVES.

HISTORICAL REVIEW OF WORK ON ADHERENCE.

The fact that it is necessary for the fungicide to adhere to the surface of the plant in order to protect it from disease has led to many investigations of the comparative adhesiveness of different copper fungicides, both with and without added adhesives. The effects of added adhesives have been tested on potatoes by Girard;[2] on wheat and other cereals by Galloway;[3] on grapes by Perraud,[4] Guillon and Gouirand,[5] Cazeneuve,[6] Gastine, [7] Chuard and Porchet,[8] and others. General studies on the adhesiveness of fungicides have been made by Kelhofer,[9–10] and various other writers. Some of the compounds used as adhesives are soap, glue, cane sugar, dried blood, gelatin, and colophene. The compounds used in the present investigation to increase adhesiveness have all been tried by other investigators, with somewhat varied results. Sirrine[11] in his work on asparagus rust recommends the use of a rosin Bordeaux mixture,

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[1] Lutman, B. F. The Covering Power of the Precipitation Membranes of Bordeaux Mixture. Phytopathology, vol. 2, February, 1912, pp. 32–41.

[2] Girard, A. Recherches sur l'adhérence aux feuilles des plantes, et notamment aux feuilles de la pomme de terre, des composés cuivriques, destinés à combattre leur maladies. Comptes Rendus de l'Académe des Sciences, vol. 114, 1892, pp. 234–236.

[3] Galloway, B. T. Experiments with Treatment of Rusts of Wheat and Other Cereals. Journal of Mycology, vol. 7, 1893, pp. 195–226.

[4] Perraud, Joseph. Moynes d'augmenter l'adhérence des bouillies cupriques sur les raisins. Journal d'Agriculture Pratique, vol. 62, pt. 2, 1898, pp. 814–816.

[5] Guillon, G. M., and Gouirand, G. Sur l'adhérence de rouillies cupriques utilisées pour combattre les maladies cryptogamiques de la vigne. Comptes Rendus de l'Académie des Sciences, vol. 127, 1898, pp. 423–424.

[6] Cazeneuve, Paul. La bouillie bordelaise albumineuse. Revue de Viticulture, vol. 9, 1898, pp. 279–280.

[7] Gastine, G. Les préparations cupriques et leur adhérence. Bulletin Mensuel de l'Office de Renseignements Agricoles, vol. 5, 1906, pp. 595–603.

8 Chuard, E., and Porchet, F. L'adhérence des bouillies cupriques. Revue de Viticulture, vol. 24, 1905, pp. 33–37.

[9] Kelhofer, W. Ueber einige Gesichtspunkte bei der Herstellung der Bordeauxbrühe. Zeitschrift für Pflanzenkrankheiten, vol. 18. Internationaler Phytopathologischer Dienst, vol. 1, no. 3, 1908, pp. 65–73.

[10] ——— Ueber die Ausführung und die Ergebnisse von Haftfestigkeitsversuchen kupferhaltiger Bekämpfungsmittel gegen die Peronospora. Zeitschrift für Pflanzenkrankheiten, vol. 17, 1907, pp. 1–12.

[11] Sirrine, T. A. Spraying for Asparagus Rust. Bulletin 188, New York Agricultural Experiment Station, 1900.

prepared by adding to the Bordeaux mixture a soap made from rosin, fishoil, and potash. Chester[1] used a rosin Bordeaux mixture in spraying grapes and asparagus, and in referring to the grape-spraying experiments says "rosin soap added to Bordeaux mixture offered no advantage over the plain mixture." He, however, considered it of value in spraying asparagus. Shear[2] used rosin-fishoil soap with good effect in spraying cranberries. Wilson and Reddick[3] used a soap in spraying grapes in 1908. In a report of their work they say, "The different 'stickers,' such as rosin sal soda, or fishoil soap, are of no practical value." Rosin-fishoil soap was used in grape-spraying experiments carried on by the United States Department of Agriculture during the years 1907 and 1908[4] without definite results. Experiments were continued in 1909,[5] however, and considerable benefit was ascribed to its use. Iron sulphate has been recommended by Selby.[6] Glue was first used by Perraud,[7] and has since been employed from time to time by cranberry growers. From the investigations here mentioned it seemed probable that the adhesiveness of Bordeaux mixture on parts of certain plants might be increased by the addition of certain compounds, though from the varied results obtained by the different investigators the relative values of these adhesives were not definitely known. An investigation was accordingly undertaken to determine, if possible, the adhesiveness of Bordeaux mixture prepared according to several formulas, together with the value of certain adhesive compounds. It was also considered worth while to try to find some laboratory method for measuring the comparative adhesiveness of these mixtures.

EXPERIMENTS ON ADHESIVENESS.

Experiments with adhesives were carried on in connection with spraying experiments for the control of the black-rot of the grape near Vineland, N. J., in the vineyard of the Vineland Grape Juice Co., during the season of 1910, and at Paw Paw, Mich., in the vineyard of Mr. Roy L. Tuttle, in 1911.

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[1] Chester, F. D. Fungous Diseases in Delaware, Part II. Treatment of Certain Plant Diseases. Bulletin 63, Delaware College Agricultural Experiment Station, February, 1904.

[2] Shear, C. L. Cranberry Spraying Experiments in 1905. Bulletin 100, pt. 1, Bureau of Plant Industry, U. S. Dept. of Agriculture. 1906.

[3] Wilson, C. S., and Reddick, D. The Black-Rot of the Grape and Its Control. Bulletin 266, Cornell University Agricultural Experiment Station. 1909.

[4] Shear, C. L., Miles, George F., and Hawkins, Lon A. The Control of Black-rot of Grape. Bulletin 155, Bureau of Plant Industry, U. S. Dept. of Agriculture. 1909.

[5] Hawkins, Lon A. Grape-Spraying Experiments in Michigan in 1909. Circular 65. Bureau of Plant Industry, U. S. Dept. of Agriculture. 1910.

[6] Selby, A. D. Modifications of Bordeaux Mixture. Sixty-second Annual Report of Ohio State Board of Agriculture, 1907, pp. 896–898.

[7] Perraud, Joseph. Op. cit.

Experiments on Adhesiveness to Grape Leaves.

The mixtures used in the experiments on grape leaves were as follows:

4-3-50 Bordeaux mixture.
4-2-50 Bordeaux mixture.
4-3-50 Bordeaux mixture with 2 pounds of ferrous sulphate to 50 gallons.
4-3-50 Bordeaux mixture with 2 pounds of rosin-fishoil soap to 50 gallons.

All mixtures were made up by diluting the copper sulphate and calcium hydroxid each to half the volume of fungicide required, and allowing them to flow simultaneously into the tank of the sprayer. The adhesives were added as follows: The fresh solution of ferrous sulphate was added to the diluted solution of copper sulphate, as recommended by Selby; the required amount of soap was dissolved in a small quantity of water and poured into the Bordeaux mixture after it had been mixed.

A portion of a 5-year-old Concord vineyard, in which the vines were apparently uniform, was divided into four plats, each plat being sprayed with one of the mixtures mentioned. The fungicides were applied with a gasoline-power sprayer. Trailers, lines of hose with short extension rods attached so that the nozzles could be manipulated by hand, were used in all sprayings. Care was taken in the application of the fungicide to see that all the sprayed plats received as nearly as possible the same quantity of the fungicide at any one application and that it was applied under the same pressure. The plats were sprayed four times, and samples of the leaves were collected after the first application and both before and after each succeeding application. Other collections were made at intervals, as shown in Table III.

The method of collecting these samples was as follows: From each plat 40 or more leaves which appeared to represent the average condition of the foliage in the plat in regard to quantity and distribution of the fungicide upon the leaf surfaces were collected at the same time. These collections were immediately taken to the laboratory, the petioles removed, the leaves with holes in them or other imperfections discarded, and the outlines of 30 to 40 leaves traced on paper. The samples were then stored in large envelopes to dry. The tracings were filed away and the area of the leaves determined later by means of a planimeter or by the weighing method. By using this number of leaves for a sample and with this method of determining the area it was considered that the quantity of copper found on the leaves would be proportional, within a reasonable percentage of error, to the quantity of copper on the leaves in the entire plat.

Later the dried leaves of a sample were removed from the envelope, placed in a casserole, and treated with sulphuric acid to convert the copper on the leaves to sulphate. They were then ashed with a Bunsen burner. The ash was extracted with dilute sulphuric acid, thrown on a filter, and washed free from copper. The copper in the filtrate was determined electrolytically. The area of the leaves as found was multiplied by two to take into account both leaf surfaces, and the amount of metallic copper calculated per square meter of leaf surface. The results of the experiment are shown in Table III.

TABLE III.—*Results of tests showing the adhesiveness of Bordeaux mixture to grape leaves. The number of milligrams of metallic copper to a square meter of leaf surface is shown.*

Plat No.	Mixture.	Date of collection.											
		May 26.[1]	June 14.[2]	June 15.[3]	June 16.[4]	July 13.[5]	July 14.[6]	July 31.[7]	Aug. 1.[8]	Aug. 11.	Aug. 18.	Aug. 26.	Sept. 5.
1	Bordeaux mixture (4-3-50)	103.8	57.7	75.4	......	29.2	60.8	45.6	70.5	67.4	64.3	57.8	16.8
2	Bordeaux mixture (4-2-50)	142.0	......	128.4	64.0	37.1	59.6	37.4	68.0	64.6	63.1	58.4	35.8
3	Bordeaux mixture (4-3-50) + ferrous sulphate	191.1	130.4	121.1	87.7	29.1	68.6	29.3	75.8	64.2	55.3	50.1	40.9
4	Bordeaux mixture (4-3-50) + soap	264.0	149.8	143.6	90.9	64.3	65.7	23.7	81.8	80.4	76.3	62.3	46.6

[1] After first application.
[2] Before second application.
[3] After second application.
[4] Next day after a rain.
[5] Before third application.
[6] After third application.
[7] Before fourth application.
[8] After fourth application.

From Table III it is apparent that there was no considerable variation in the adhesiveness of the different mixtures throughout the season, though usually a little more copper per unit area was found on the samples of leaves from the plat sprayed with Bordeaux mixture to which the rosin-fishoil soap had been added. Immediately after the first application the increased adhesiveness of the rosin-fishoil soap mixture is very marked, but in samples collected after the third application a little more copper per unit area was found on samples from some of the other plats. On the whole, however, the addition of rosin-fishoil soap may be said to be of some slight benefit in increasing the adhesiveness of Bordeaux mixture to grape leaves.

It is apparent that in some cases the quantity of copper on the leaves after spraying was less than that found on the sample collected just before the same application, as before and after the second application in the plat sprayed with the ferrous-sulphate mixture. This is due to the fact that collections before spraying were made only of the leaves which had been sprayed in the previous application, while in collections made after an application leaves of all stages of growth were collected.

Some data on the effect of a rain on the adhesiveness of the spray mixture are given under the dates June 15 and 16 in Table III. The usual collection of leaves was made immediately after the second spraying, and about three hours after this application rain fell, the precipitation being 0.71 inch. Leaves were collected the following day, and from these samples the results under date of June 16 were obtained. The amount of copper on the leaves decreased 35 to 50 per cent by reason of the growth of the leaves during 18 hours and the removal of the copper by the rain. Data for plat 1 are unfortunately lacking.

No evidence is found in these experiments to verify Kelhofer's[1] suggestion that Bordeaux mixture with a large excess of lime adheres to the leaves for a longer time than the more nearly neutral mixture. The percentage of copper removed from the leaves in a given time after spraying with the 4–2–50 or 4–3–50 Bordeaux mixture varies only slightly. The growth of the leaves increasing the leaf area makes it impossible to secure accurate data on the quantity of copper actually removed from the leaves, but as the vines in these plats were the same to all appearances and the same method of sampling was used it is probable that the results are comparable.

Experiments on Adhesiveness to Grape Berries.

It was observed in the course of the preceding experiment that while all the mixtures adhered fairly well to the leaves there was considerable difference in their adhesiveness to the grape berry if the berry was covered with bloom. In spots on the berry from which the bloom had been removed, however, there seemed to be no marked difference in the quantity of fungicide present. When the grapes covered with this bloom were treated with Bordeaux mixture to which no adhesive compounds had been added the mixture seemed to run off immediately or round up into little droplets and hang at the lowest point of the fruit.[2] On the other hand, if the rosin-fishoil soap had been added, the mixture formed a film, completely covering the berry. From these observations it was concluded that the adherence of a fungicide to the leaves was no guaranty of its adherence to the fruit. In order to get accurate data upon the subject it was necessary to carry the experiments further, paying special attention to the fruit.

This investigation on the adhesiveness of the fungicide to the grape berries was carried on at Paw Paw, Mich., in 1911. More

[1] Kelhofer, W. Ueber einige Gesichtspunkte bei der Herstellung der Bordeauxbrühe, Zeitschrift für Pflanzenkrankheiten, vol. 18. Internationaler Phytopatholigischer Dienst, vol. 1, no. 3, 1908, pp. 65–73.

[2] Perraud, op. cit., p. 815, noticed this difference in the adhesiveness of Bordeaux mixture on the leaves and berries in his investigations and remarks, " La faculté d'adhérence des bouillies cupriques est beaucoup plus faible pour les raisins que pour les feuilles de vigne."

adhesive compounds were used in this experiment than in that with the leaves, and the concentration of some of the adhesives was varied. Eight plats of Concord grapes were sprayed four times in the experiment with the following mixtures:

Plat 1. 4–3–50 Bordeaux mixture.
2. 4–3–50 Bordeaux mixture, with 2 pounds of ferrous sulphate.
3. 4–2–50 Bordeaux mixture.
4. 4–2–50 Bordeaux mixture, with 2 pounds of rosin-fishoil soap.
5. 4–2–50 Bordeaux mixture, with 1 pound of rosin-fishoil soap.
6. 4–2–50 Bordeaux mixture, with 2 pounds of fishoil soap.
7. 4–2–50 Bordeaux mixture, with 2 pounds of ground glue.
8. 3–2–50 Bordeaux mixture, with 2 pounds of rosin-fishoil soap.

The soap and the ferrous-sulphate mixtures were prepared as in the experiment already described, and the glue (a dry, ground glue) was dissolved in a small quantity of hot water and added to the Bordeaux mixture. The mixture was prepared as in the preceding experiment.

The mixtures were applied with a steam sprayer, and, as in the work in 1910, care was taken to see that as nearly as possible the same quantity of mixture was applied under the same pressure to each plat. Collections of grape berries were made from each plat immediately after the last spraying, a similar system of sampling being employed as in the experiment with leaves the preceding year. In this case, however, duplicate samples were collected from each plat. Each sample consisted of about 500 grapes, which were cut from the pedicels, the diameter measured to tenths of a millimeter, and the berries stored to dry. The total area of the grape surfaces in each sample was calculated from the diameters of the individual grapes, as the berries were approximately spherical. Later, the copper on the grapes was determined, as in the preceding experiment with the leaves, and related to the square-meter grape surface for each sample. Through an accident in ashing, the data for one sample from plat 7 are lacking. A second collection was made five weeks after the first and treated in the same way. The quantity of copper on the individual samples was so small in this case that it was impracticable to attempt to compare the data from the different plats. Three milligrams was the greatest weight of copper found on any sample in this last series. The weight of copper on grapes immediately after the fourth application is shown in Table IV under "Weight of copper," etc.

SURFACE TENSIONS OF MIXTURES USED.

In the course of the experiment on the leaves it was found that the mixtures with the lowest surface tension seemed to adhere best to the fruit, i. e., the Bordeaux mixture to which the rosin-fishoil soap had been added, thereby lowering the surface tension, seemed to adhere much more tenaciously to the bloom-covered fruit than

the mixture without the added adhesive. This is in accordance with the results of the work of Vermorel and Dantony[1] on the adhesiveness of certain fungicides to grape berries. These authors found in their investigations that the addition of soap to the mixture lowered the surface tension, and that the mixture with the lowest surface tension wet the grape berries best.

With a view to discovering any existing relation between the surface tension of the mixture and its adhesiveness to the bloom-covered grape, surface-tension measurements were made of all the mixtures used in the experiments in 1911. For these measurements a spring balance of the Joly type, provided with a loop of 36-gauge German-silver wire, was used. This loop consisted of a piece of wire with both ends bent down at right angles to the straight middle portion, which was about 5 centimeters long. When in use, the middle portion of the loop was parallel to the surface of the liquid, the ends being perpendicular to this surface and extending below it. To determine the surface tension of a mixture the loop was first weighed with the ends thrust into the liquid and the middle portion at a given height, usually about 8 millimeters above the surface. The loop was then dipped into the liquid and weighed again with a film of the liquid held in the loop. The difference in weight with and without this film was considered to be the weight of the film.

While taking these measurements the fungicide was contained in a crystallizing dish of convenient size on the stand of the apparatus. As the same loop was used in all measurements and at the same height above the surface of the liquid in each test, these weights should have the same relation to each other as the surface tensions of the liquids. The weights for samples of the Bordeaux mixtures used in spraying the different plats are given in column 4 of Table IV. The measurements are, of course, not of the highest degree of accuracy, yet they were made at nearly the same time, at the same temperature, and with all other conditions as nearly alike as possible, and should therefore be comparable.

If the increased adhesiveness of the fungicide to the bloom of the grape is due to the lowering of the surface tension of the liquid, as might seem to be the case from the results obtained in 1910 in this investigation and from the work of Vermorel and Dantony, the surface tensions should be inversely proportional to the adhesiveness of the Bordeaux mixture found by determining the copper on the grape berries. From Table IV it may readily be seen that such is not the case. No. 4, in which 2 pounds of rosin-fishoil soap were added to the mixture, adhered best and had the lowest surface tension, while in No. 5, where half the quantity of the same soap was

[1] Vermorel and Dantony. Sur les bouillies anticryptogamiques mouillantes. Reveu de Viticulture, vol. 35, 1911, pp. 493–494.

used and which had practically the same surface tension, the quantity of copper on the berries was about two-thirds that found in No. 4. No. 6, in which 2 pounds of fishoil soap was added to the Bordeaux mixture, had the next lowest surface tension, but only about one-fourth as much copper to the unit area was found on the berries as in No. 4. No. 7, the glue mixture, which had the highest surface tension of any of the mixtures to which adhesives were added, except No. 3, most nearly approached No. 4 in adhesiveness. As may be seen from Table IV, no increased adhesiveness of the fungicide resulted from the addition of ferrous sulphate. In the samples of grapes from the plat sprayed with this mixture, as well as those from the two plats on which Bordeaux mixtures without added adhesives were used, there was not sufficient copper present for accurate determination. The results of these experiments show clearly that the adhesiveness of the spray mixtures is not to be related directly to the depression of their surface tensions,[1] but that some other factor must be taken into account.

A Laboratory Method for Comparing the Efficiency of Added Adhesives.

In the method used for measuring the surface tension of the mixtures a surface was employed which was wet by the liquid, while the waxy coating of the grape under usual conditions is not wetted by ordinary Bordeaux mixture. Experiments to prove this point were made by weighing grapes covered with bloom and dipping them into Bordeaux mixture to which no adhesives had been added and again immediately weighing them. In hundreds of tests the weights before and after the immersion did not vary as much as a milligram. But when grapes were immersed in Bordeaux mixture to which 2 pounds of rosin-fishoil soap to 50 gallons of mixture had been added, a film of the liquid was formed over the surface in every case and the weight was increased 26 to 80 milligrams by the mixture adhering to the surface.

From these experiments a method of measuring the relation of the liquid to the bloom of the grape itself was suggested. Strips of grape skin 2 to 3 millimeters in width and 20 to 40 millimeters in length were cut from the surface of the grapes. When these were peeled off they immediately rolled up in a comparatively straight rod about a millimeter in diameter, with the external surface of skin on the outside. This rod was thrust into the mixture to be tested, which was contained in a crystallizing dish on a convenient stand, and the depression of the surface of the liquid next to the rod was measured by means of a horizontal microscope with a micrometer ocular.

[1] Some months after this manuscript was submitted for publication, an article by Vermorel and Dantony came to the writer's notice, in which they reach the conclusion that the wetting power of a mixture is not related directly to the lowering of the surface tension. (See Vermorel, V., and Dantony, E., "Tension superficielle et pouvoir mouillant des insecticides et fongicides," Revue de Viticulture, vol. 37, 1912, pp. 715–716.)

A series of such measurements of Bordeaux mixture with and without the added adhesives was made, and it was found that the measurements related in a rough way to the amount of copper found in the determination of the copper on the grapes. That is, the mixture which adheres best to the surface of the grape is depressed the least and that which adheres least is depressed the most. The other mix-

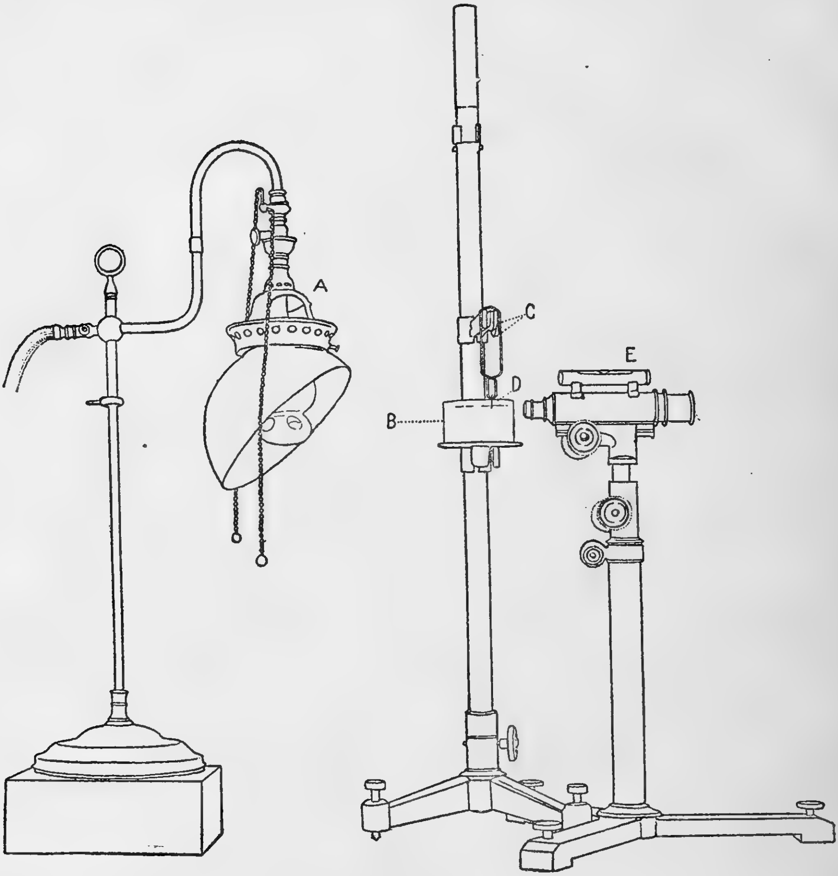

Fig. 3.—Sketch of apparatus used for measuring the depression of the surface films of Bordeaux mixture by the bloom of the grape. *A*, Source of light (Welsbach lamp); *B*, crystallizing dish containing mixture on apparatus stand; *C*, cover-glass forceps for holding roll of grape skin; *D*, roll of grape skin thrust partly below surface of liquid; *E*, horizontal microscope. The roll of grape skin *D* is placed so that the long axis is perpendicular to the liquid surface and the roll extends a little below this surface. The depression of the liquid surface next to the grape skin is then measured with the micrometer eyepiece of the horizontal microscope.

tures with added adhesives are grouped between these two extremes in the order of their value as determined by the amount of copper on the grapes. The method of measuring this depression is illustrated in figure 3. The average of a large number of measurements of Bordeaux mixture without added adhesives and with the four adhesives which proved of value are shown in Table IV under "De-

pression of surface of mixture." A diagram of the comparative depression of mixtures with the 2 pounds of rosin-fishoil soap and without additional adhesives is shown in figure 4. In making the

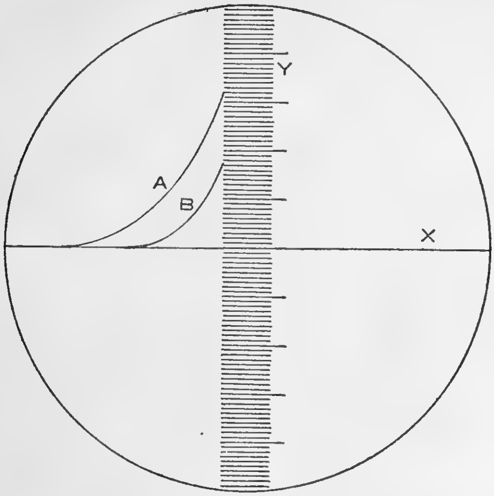

FIG. 4.—Diagram which compares the average depressions as seen in horizontal microscope of the surface films of Bordeaux mixture without added adhesive and Bordeaux mixture with 2 pounds of rosin-fishoil soap to 50 gallons of mixture. *X*, Median line of eyepiece micrometer which coincides with the surface of the mixture in crystallizing dish; *Y*, graduated scale of micrometer eyepiece; *A*, average depression of surface film of 4–2–50 Bordeaux mixture without added adhesives by the bloom of the grape; *B*, average depression of surface film of 4–2–50 Bordeaux mixture with 2 pounds of rosin-fishoil soap to 50 gallons of mixture.

measurements given in Table IV the mixture was always well agitated beforehand to stir up the precipitate and break up the film of calcium carbonate which formed on the surface.

TABLE IV.—*Results of tests showing the adhesiveness of Bordeaux mixture to grape berries alone and with various added adhesives, as shown by the quantity of copper on the berries, the comparative surface tension of various mixtures used as found by weight of a film of the mixture, and the depression of the surface of the mixture by the bloom of the grape.*

Plat No.	Mixture.	Weight of copper to a square meter of grape surface.			Weight of loop of mixture.	Depression of surface of mixture.
		Sample A.	Sample B.	Average.		
		Milligrams.	*Milligrams.*	*Milligrams.*	*Milligrams.*	*Millimeter.*
1	4-3-50 Bordeaux mixture	Trace.	Trace.	....	726	....
2	4-3-50 Bordeaux mixture with 2 pounds of ferrous sulphate	Trace.	Trace.	....	731	....
3	4-2-50 Bordeaux mixture	Trace.	Trace.	....	737	0.9442
4	4-2-50 Bordeaux mixture with 2 pounds of rosin-fishoil soap	24.5	30.3	27.4	499	.4980
5	4-2-50 Bordeaux mixture with 1 pound of rosin-fishoil soap	18.9	16.4	17.65	490	.6260
6	4-2-50 Bordeaux mixture with 2 pounds of fishoil soap	5.6	7.6	6.6	593	.6691
7	4-2-50 Bordeaux mixture with 2 pounds of ground glue	19.9	....	19.9	691	.6002
8	3-2-50 Bordeaux mixture with 2 pounds of rosin-fishoil soap	14.7	13.2	13.85	488	....

DISCUSSION OF THE RESULTS OF THE EXPERIMENTS.

The results of the experiments in preparing Bordeaux mixture detailed in the foregoing pages show that the rate of subsidence of the suspension is not dependent on the way in which the two components are brought together, provided one is dilute. It should be possible in practice to place the proper quantity of copper-sulphate solution or lime paste in the spray tank, dilute it with water to nearly the quantity of fungicide desired, and then to add the other component in a concentrated form. By vigorous agitation this should, according to the experiments described here, furnish a suspension which settles out as slowly as in any other common method of preparation. (See figs. 1 and 2 and Tables I and II.) This method of preparation should be useful in spraying cranberries. The conditions in this work are frequently such as to make impracticable the erection of raised platforms for mixing. It must be remembered that, with this method of mixing, good results were obtained only when the mixture was thoroughly agitated. The agitation was much more vigorous in the laboratory experiments than is usually obtained with the common barrel-pump outfit.

The addition of cane sugar to Bordeaux mixture to decrease the rate of subsidence, as Kelhofer and Kulisch suggested, was not tested. As these writers point out, it would probably be useful under certain conditions for persons using a small quantity of Bordeaux mixture from time to time. However, in commercial work in which Bordeaux mixture can be conveniently prepared and used immediately the addition of sugar would seem to entail an unnecessary expense. The method suggested by Pickering of preparing Bordeaux mixture by mixing the copper sulphate solution with a saturated solution of calcium hydroxid makes a suspension of the copper compound which settles out very slowly. It is doubtful whether this method would be practicable in the preparation of the large quantities of fungicides required for spraying in a commercial way. It would be impossible to prepare a neutral Bordeaux mixture containing three-fourths to 1 per cent of copper sulphate by this method, as a saturated solution of calcium hydroxid does not contain enough lime to react with the amount of copper salt in a solution of this concentration. The mixture might be prepared and the precipitate allowed to settle and enough of the supernatant liquid drawn off to leave a mixture of the proper concentration. This process would of course add greatly to the cost of spraying. It is possible that a smaller percentage of copper sulphate might be as effective as three-fourth to 1 per cent. From the evidence at hand, however, this conclusion would hardly be warranted.

Of the adhesive compounds added to Bordeaux mixture, the rosin-fishoil soap proved to be most effective on the grape berries—much more effective, in fact, than fishoil soap without the rosin. From this fact it seems probable that the adhesiveness is largely due to the rosin present. It is stated by various writers that the addition of a small quantity of soap to Bordeaux mixture could be of no particular benefit, as the soap would be precipitated as an insoluble calcium soap by the excess of calcium present in the mixture. Good results could therefore be expected only when a considerable quantity of soap was added. This, of course, may be true of certain kinds of soap, but in this investigation considerable benefit was derived from the addition of relatively small quantities of soap. Even the fishoil soap materially increased the adhesiveness over Bordeaux mixture without added adhesives.

In the treatment of the black-rot of the grape good results have been obtained in many cases by using Bordeaux mixture without added adhesives. When we consider this fact in connection with the evidence brought forth in the present investigation, that Bordeaux mixture without added adhesives does not adhere to the grape berry in any appreciable quantity, it seems probable that the protection is due to reducing the sources from which infection comes to the berry. By protecting the foliage from infection the possibility of secondary infection from the foliage to the fruit may be eliminated to a considerable extent. Covering the stems of bunches of grapes with the fungicide seems to be another means by which infection may be kept from the grapes. The writer has observed numerous instances of black-rot infection on bunches of grapes which had been bagged six weeks or more. In these instances spores probably washed down the stems in drops of water, as the only openings in the bags were immediately around the stems.

Though good results were obtained by the addition of glue to Bordeaux mixture, its cost (about 12 cents a pound) prohibits its use in commercial work in place of rosin-fishoil soap. When glue is added to alkaline Bordeaux mixture, part of the copper combines with the glue, forming a soluble compound bright purple in color. It is probable that much of the copper found on the grapes from this plat was in this form. As it is soluble in water, this protective covering might not remain on the berries as long as the insoluble precipitates in the mixtures with the soap.

It is difficult to see in just what way ferrous sulphate could be expected to influence the adhesiveness of Bordeaux mixture. On the addition of this compound to a solution of calcium hydroxid, ferrous hydroxid immediately precipitates out, and none of the

ferrous sulphate remains in solution. It was found to be worthless as an adhesive for use on grapes.

In the plats sprayed with 3–2–50 Bordeaux mixture, to which was added 2 pounds of rosin-fishoil soap, a considerable quantity of copper was found on the grapes. This formula has given excellent practical result and should prove much more effective than the mixtures containing more copper but without the adhesive.

CONCLUSION.

It has been shown in these investigations that a Bordeaux mixture in which the suspension of the copper compound settles out slowly may be prepared by adding the concentrated calcium hydroxid to the diluted copper-sulphate solution or vice versa, provided the mixture is sufficiently agitated. Practically as good results were obtained with these methods of preparation as by diluting the two components in separate vessels and pouring them simultaneously into a third, as recommended by Galloway in 1896.

It is to be remembered that in preparing Bordeaux mixture, by pouring one of the components in concentrated form into the other diluted to nearly the required volume, the resulting mixture must be thoroughly agitated. The agitation necessary for preparing Bordeaux mixture with a low rate of subsidence by this method could hardly be obtained in practice except by means of a power outfit provided with a good agitator. This method of mixing is not designed to replace the old gravity method with its elevated platform, but offers a convenient substitute where for any reason the gravity method is impracticable.

In the experiments on the adhesiveness of certain Bordeaux mixtures and the relative value of certain adhesive compounds it was shown that by determining the quantity of copper retained on the leaves sprayed with the different mixtures the addition of rosin-fishoil soap slightly increases the adhesiveness of the mixture. In similar experiments on grape berries it was shown that the adhesiveness of the fungicide could be materially increased by the addition of certain adhesive compounds. Two pounds of rosin-fishoil soap to 50 gallons of spray mixture was the most valuable of any added adhesive, ground glue was second, 1 pound of rosin-fishoil soap to 50 gallons of mixture was third, and fishoil soap was fourth. Ferrous sulphate did not increase the adhesiveness of the Bordeaux mixture, as no appreciable quantity of copper adhered to the grape berries where the Bordeaux mixture to which the ferrous sulphate had been added was used. No appreciable quantity of copper was found on the grape berries from the plats sprayed with Bordeaux mixture without added adhesives. From the experiments on grape

berries with adhesives it may be concluded that the use of an adhesive compound is necessary to make the fungicide adhere to the bloom-covered grapes. Two pounds of rosin-fishoil soap to 50 gallons of mixture gives the best results and is recommended as the most economical and efficient adhesive for use on grape berries. From the results obtained with 3–2–50 Bordeaux mixture, with the addition of soap, it seems probable that a mixture containing this quantity of copper sulphate would be effective when a good adhesive is used. A laboratory method of approximating the relative adhesiveness of these fungicides to grapes was developed.

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